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Dielectric properties of lead zirconatetitanate

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Ferroelectric lead zirconate titanate (PZT) thin films deposited on metal foil substrates are suitable for developing a wide range of applications. PZT were prepared by mixed oxide method at 1100°C. Crystalline nature of the synthesized PZT has been confirmed by X-ray powder diffraction studies. Dielectric measurement shows that decrease in dielectric constant with increase in temperature. The dielectric loss was found to be very small and decreasing with frequency, also above 300°C. The increase of dielectric constant observed at high temperatures and low frequencies in the paraelectric state are explained.

Keywords: Ferroelectricity, PZT, Dielectric constant, Calcination, Sintering, Porosity

Introduction

Lead zirconate titanate solid solutions, Pb ($Zr_{1-z}Ti_z$)O_3, are widely recognized to represent a special group of perovskite-type A(B′B″)O_3 ferroelectric materials with various potential applications in electro ceramic and (micro) electronic devices, e.g. as high permittivity capacitors, piezoelectric elements, pyroelectric detectors and ferroelectric memories[1]. Even though lead zirconate titanate, Pb(Zr.Ti) O_3(PZT), solid solutions were first reported in 1952[2,3], real interest in PZT was drawn by the discovery of a peak in the dielectric[4] and piezoelectric properties[5-7]for compositions close to 52 mol% of $PbZrO_3$ (PZ) by Jaffe, Roth and Marzullo[8]. Researchers have reported lot of work on the synthesis of PZT thin films and ceramics[9-13].

Since the possibility of preparing a wide range of composition of solid solutions of required size, the use of polycrystalline or ceramics materials is being of particular purposes. The ferroelectric behavior of ceramics depends greatly on the crystallite size, which can be controlled during preparation by varying the firing temperature, atmosphere, sintering time and composition of the solid solution[14]. It is therefore, proposed to prepare the solid solutions of doped Pb(ZrTi)O_3 and different compositions.

Synthesis of Samples

In order to prepare the solid solutions of doped Pb(ZrTi)O_3, following analytical reagent (AR) chemicals have been used:

PbO (lead oxide), TiO_2 (titanium dioxide), and ZrO_2 (zirconium dioxide).

The term solid-state synthesis has been used to describe interactions, where neither a solvent medium nor controlled vapor-phase interactions are utilized. Since these reactions often involve extreme conditions (high temperature and/or high pressure). Solid-state synthesis has been used to create the unique compositions and morphologies needed to generate the desired attributes in scintillation crystals, piezoelectric, and other advanced materials.

Using this method, we have to prepare modified Lead Zirconate Titanate by conventional solid-state reaction method, which employs series of mixing, grinding with varying temperature and times of heating schedule.

The raw materials (metals oxides and metal carbonates) were first weighed according to the stoichiometric formula of the desired ferroelectric ceramic as proposed by following compounds:

$Pb_{1-x}\ La_x\ (Zr_y\ Ti_{1-y})_{1-x/4}\ O_3$; where x= 0, 0.03; y=0.70

The raw materials should be of high purity. The particle size of the powder must be in the sub-micron range for the solid phase reaction to occur by atomic diffusion. Then these materials were mixed for 50 to 60 minutes with the help of "AGAT MORTAR" in the medium of acetone. Mixing is done to make the mixture homogenous.

All the homogeneously mixed samples were calcined at 1000 °C for 2 h. Calcination is

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necessary for the completion of solid-state reaction. To check the formation and phase purity of the required samples XRD of the calcined powder was done. Then five pellets of each sample were formed with the help of uniaxial hydraulic press and die punch. Pellets were sintered at 1100 °C for 4 h and 6 h. Sintering is done to reduce porosity and make pellet more compact.

Results and Discussion

The aim of the research described in this paper is focused on the preparation and characterization of pure/modified $Pb(ZrTi)O_3$. The X-ray diffraction (XRD) patterns of Pb_{1-x} La_x $(Zr_y$ $Ti_{1-y})$1-x/4 O3;wherex=0,0.03;y=0.70 compounds are shown in Figs. 1 and 2.

Absence of the triplets in the XRD patterns of Figs. 1 and 2 indicates that there is no coexistence of ferroelectric phases in the entire range of modified compositions. Absence of the coexistence region can be attributed to the greater chemistry homogeneity of the prepared powders, which restricts compositional fluctuations in the sintered ceramics. All the reflections peaks of the samples were indexed using a standard computer program[15].

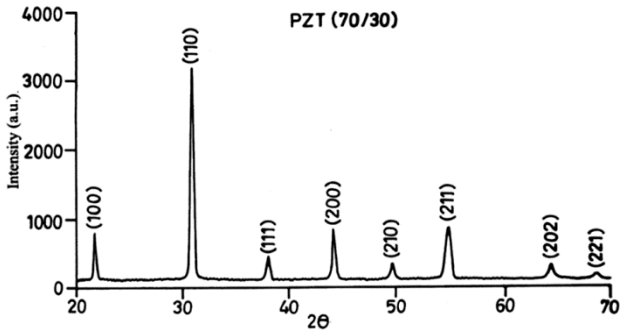

Fig. 1 — X-ray diffraction pattern of $Pb(Zr_{0.7}Ti_{0.3})O_3$ at 1100°C, 4 hours in presence of $PbZrO_3$.

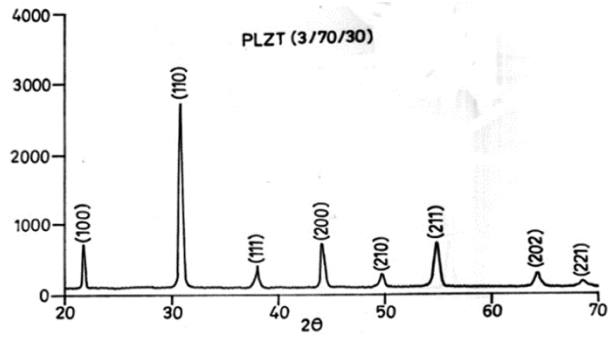

Fig. 2 — X-ray diffraction pattern of $Pb_{0.97}(Zr_{0.7}Ti_{0.3})O_3$ at 1100°C, 4 hours in presence of $PbZrO_3$.

The preliminary X-ray analysis indicates that the specimens were of rhombohedral structure. By increasing the concentration from x=0 to x=0.3, a very small difference in the d-value have been observed but keeping the final structure invariant however, a systematic change in intensity of the few reflections have been observed. This change in intensity may be due to (i) variation of particle size and (ii) presence of dopants in different amount.

Dielectric Measurement

The variation of dielectric constant (ε) and tanδ (dielectric loss) with frequency of all the samples at room temperature were measured in the frequency range of 10^2 Hz to 10^5 Hz. Dielectric constant (ε) and tanδ was found to decrease with increase in frequency. Generally, both of these parameters decrease with increase in frequency and hence show a typical characteristic of dielectrics (ferroelectric). The mechanism of variation in dielectric constant of the ceramic with frequency can be explained in terms of four types of polarization's which contribute to the dielectric constants of materials. These are: electronic, ionic, orientation and space charge polarization. At very low frequency (less than 10 kHz), all the contributions may be active. From the nature of the variation of ε with frequency, it is possible to find out which contributions are predominately present in the compound in a particular frequency range. In the region of frequency under investigation only the contribution of Polar Regions to the total dielectric constant undergo dispersion. All these spontaneously polarisable regions make a contribution to the dielectric constant only at temperature below the transition point. Increase in the space charge polarization of solid increases the value of ε and tanδ. This polarization arises due to defects and impurities present either in the bulk or at the surface of the crystal or both. Due to large polarization of defects in the crystals, the space charge polarization increases and thereby ε and tanδ of the crystal become high. The dipolar orientation effect can sometimes be exhibited some materials even upto10^{10} Hz. The ionic and electronic polarizations always exist above 10^{13}Hz. Only pure electronic polarization exists above 10^{15} Hz as a result of which the dielectric constant of the material falls down to a very low value.

Pressed ceramics samples generally contain voids, grain boundaries and other defects. The

presence of voids decreases the dielectric constants[16]. However, if the density of the sample approaches the single crystal value, then this effect is practically eliminated. The number of polarizable entities will be enhanced due to increase in density or packing fraction and they exhibit larger ε values. The dielectric loss in pellet samples is mostly due to the scattering mechanism[17].The scattering cross section depends upon grain size inter grain space and grain boundaries. Therefore, the loss factor decreases smoothly with increase of frequency because of high packing fraction of pellet. The smaller grain size also affects the scattering and increases the scattering amplitude. Furthermore, the space charge may arise from the charges present at the surface of the crystallites.

Figures 3-6 shows the variation of dielectric constant and tan δ as a function of temperature at different frequencies for selected samples. As for normal ferroelectrics, dielectric constant increases with increase of temperature up to transition temperature (Tc) then it decreases. It is seen that the region around the peak is broadened the broadening of the transition has been attributed to disorder in the arrangement of the cations developed in a-site which is occupied hereby $pb^{2+}$and at b-site by zr^{4+},$Ti^{4+}$and la^{3+}. This leads to a microscopic heterogeneity in the composition and thus in a distribution of different local curie points. It is also seen that Tc is independent of increase in frequency.

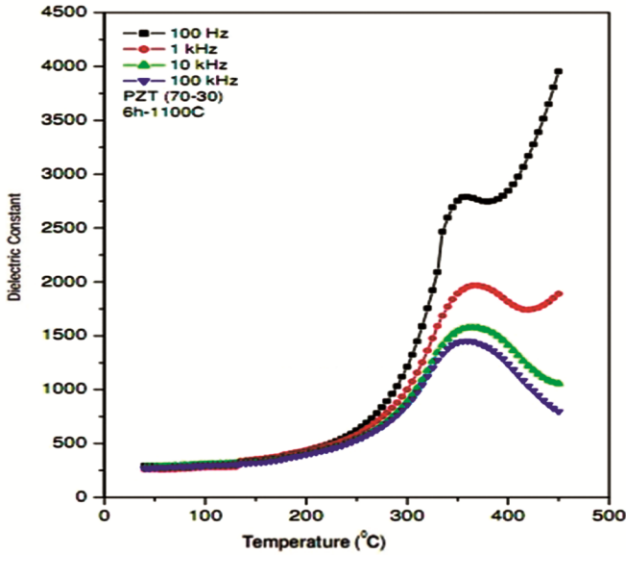

Fig. 3 — Variation of dielectric constant as a function of temperature at different frequency for PZT(70/30).

The magnitude of dielectric constant was found to be highly depending on both doping and measured frequency. Strong dispersion in dielectric constant appears to be common feature in ferroelectrics associated with non-negligible ionic conductivity and is referred to as the low frequency dielectric

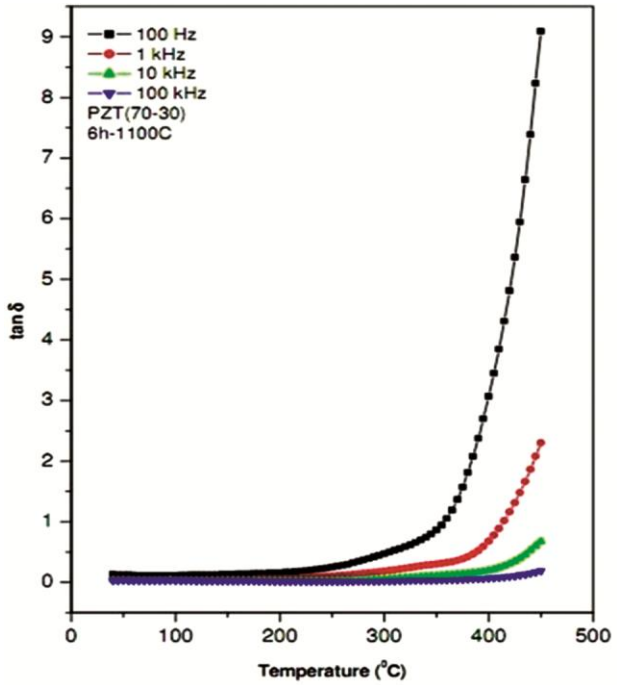

Fig. 4 — Variation of dielectric loss as a function of temperature at different frequency for PZT(70/30).

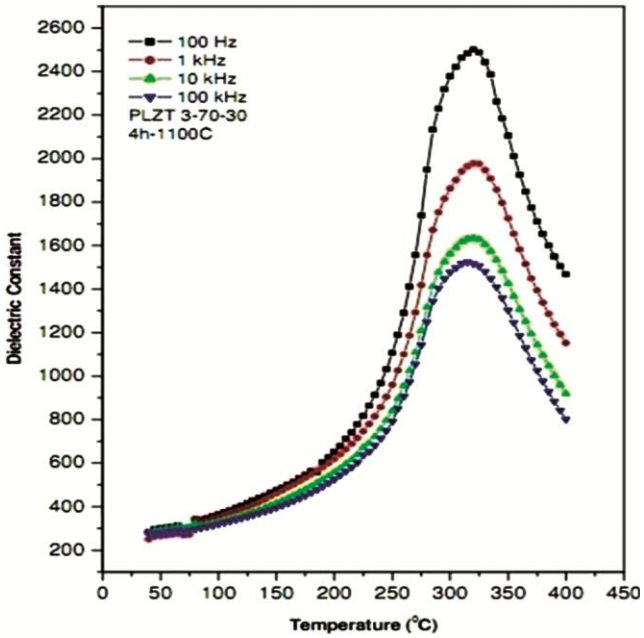

Fig. 5 — Variation of dielectric constant as a function of temperature at different frequency for PLZT(3/70/30).

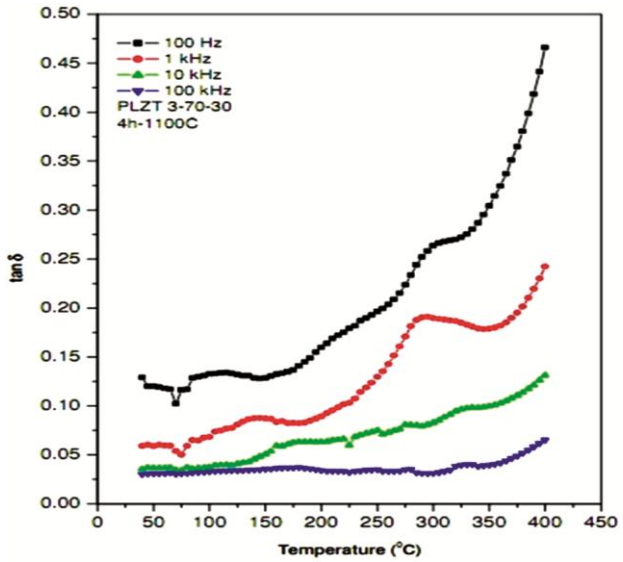

Fig. 6 — Variation of dielectric loss as a function of temperature at different frequency for PLZT(3/70/30).

dispersion (LFDD)[18-19].The dielectric loss was found to be very small and decreasing with frequency, alsoabove300°C,a sharp increase in tan δ was observed. This growth in tan δ is brought by an increase in both conduction of residual current and the conduction of absorption current. The quantitative assessments of the diffusivity (γ) and diffuseness parameter (δ) in the paraelectric phase was evaluated using the expression given by Martirena and Burfoot[20]

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_{max}} + \frac{(T - T_C)^{\gamma}}{2\delta^2}$$

where γ and δ are constants.

Conclusions

The observed single-phase rhombohedral structure implies that dopants and PZT form solid solutions over whole range of additives. As the change in d-values was found insignificant, it is concluded that the final structure is invariant. In all the compounds the regions around the dielectric peak are broadened. The broadening of the dielectric peak and decrease in the maximum value of dielectric constant values are consistent with the decrease in the grain size as the concentration of dopants increases.

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